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# DEVELOPMENT OF A MOLTEN CARBONATE PROCESS FOR REMOVAL OF SULFUR DIOXIDE FROM POWER PLANT STACK GASES

PROGRESS REPORT NUMBER 2
PART VII. PLANT ANALYSIS
April 1, 1968 to October 27, 1968

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The work upon which this publication is based was performed by Atomics International, A Division of North American Rockwell Corporation, Canoga Park, California, pursuant to Contract No. PH 86-67-128 with the U. S. Public Health Service, Department of Health, Education, and Welfare. Patents covering the basic process have been issued to North American Rockwell Corporation.

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## SUMMARY

Atomics International is continuing development of a molten carbonate process to remove sulfur oxides from power plant stack gases, under contract PH-86-67-128. In this process, the sulfur oxides are absorbed in a molten mixture of lithium, sodium, and potassium carbonates. The resulting carbonate-sulfite mixture is then regenerated chemically. Work began June 1, 1967, with effort in four major areas: process chemistry, corrosion studies, contactor development and component development. Since then, work has also been initiated on pilot plant and component test loop design, and on plant analysis. This part of the summary report describes the plant analysis results achieved through October 28, 1968.

The operating and capital costs for treating the stack gases of a 60 Mwe and an 800 Mwe power plant were estimated and evaluated. The assumptions in earlier cost estimates (Summary Report, June 1, 1967 - February 28, 1968, AI-68-104) parallel those utilized by S. Katell, et al. of the Bureau of Mines in their economic comparisons of sulfur dioxide removal processes (Chemical Engineering Progress 62 (10), 67, Oct. 1966). Changes from these assumptions were made to reflect a realistic appraisal of the molten carbonate process. These changes include additional charges for removing fly ash from the gas stream, the utilization of hydrogen gas as the reducing agent, a gas utilization factor of 80%, an equipment cost contingency of 20% and a contractor's overhead of 25%. The total cost for integrating the process with a 60 Mwe power plant, including a sulfur plant, was estimated at $3,200,000. The Watts Bar Power Plant of the TVA System was chosen for the integration consideration.

The capital requirement for an 800 Mwe installation using hydrogen as the reducer gas is estimated at $11,686,000 (14.60/kw) and an annual operating cost, at a 90% load factor, of $3,940,000 (0.622 mils/kwh). These values are 40% higher than the estimate prepared for the Summary Report, June 1, 1967 to February 28, 1968, AI-68-104. The increase is mainly caused by two factors: (1) the electrostatic precipitator penalty was increased from $1,260,000 to $3,000,000, and (2) the reduction process was evaluated for hydrogen gas instead of the earlier contemplated steam-coal producer gas. Both of these increases result in a very conservative estimate of the final costs. The high cost of the precipitator can be reduced when an economic method to recover the melt from fly ash is developed. The high cost of the reduction step, which has caused both a high capital and operating cost, can be materially reduced (40%) when a cheaper reducing agent such as carbon replaces the hydrogen gas.

Several important observations from the 800 Mwe plant analysis are summarized below:

1. The reduction step using hydrogen as the reducing agent contributes 47% of the total overall process cost.

2. The cost of natural gas as the raw material for hydrogen production is an important contributor in the overall cost of the process. If the natural gas cost increases from 40¢ to 50¢ per 1000 SCF, the overall $SO_2$ removal cost increases by $300,000 per year, or roughly 8%. The effect of reduction reaction time on the overall cost is of secondary importance.

3. Using hydrogen as the reducing agent, the overall system costs are estimated at 0.62 mils/kwh (no credit for sulfur is included).

4. Carbon (fluidized coke) as the reducing agent offers the highest potential for lowering the overall cost. Preliminary calculations show that the system cost could be reduced to 0.42 mils/kwh. The reduction step using fluidized coke would contribute only 26% to the total cost, in contrast to the step using hydrogen, which contributes 47% of the total cost. The costs were based on a reaction time of 1-3/4 hours at 1290°F. However, further investigation is required into the material technology at the higher operating temperature, the chemistry of the process, and the feasibility to supply heat during the endothermic reaction.

5. The overall costs can be reduced by 0.07 mils/kwh if a reducing mixture of 75/25 hydrogen/carbon monoxide can be effectively utilized. A further reduction of 0.04 mils/kwh can be realized by crediting reduced stack height requirements and lower corrosion due to the removal of the $SO_2$ from the flue gases.

6. Unless nearly all of the fly ash is removed (more than 99%) from the gas stream before it enters the scrubber, the carbonate melt must be recovered from the melt-ash filter cake for economic operation.

# I. INTRODUCTION

Atomics International is continuing development of a molten carbonate process to remove sulfur oxides from power plant stack gases, which is the subject of contract PH 86-67-128 with the Public Health Service, Department of Health, Education, and Welfare. In the basic process, a molten mixture of alkali metal carbonates is used to scrub the stack gases. The sulfur oxides in the stack gases react with the carbonates to form sulfites and sulfates, which remain dissolved in excess carbonate. The molten carbonate-sulfite-sulfate salt mixture is then regenerated chemically, converting the sulfite and sulfate back to carbonate and hydrogen sulfide. The carbonate is then recirculated to the scrubber to continue the process.

This report describes the results of the Plant Analysis work performed during the eight-month period ending October 27, 1968. In this analysis, a conceptual design of a large pilot plant was prepared for integration into a 60 Mwe power plant at the TVA Watts Bar, Tennessee Station and the capital and operating costs for this were estimated. A conceptual design of a prototype full size plant (800 Mwe) was also prepared, and the capital and operating costs estimated. Preliminary analysis was conducted in several key areas. These covered aspects of the integration with an existing power plant, the reduction step, the fly ash removal, and molten carbonate recovery.

# II. SYSTEM DESCRIPTION OF LARGE PILOT PLANT (60 Mwe)

## A. BASIS OF DESIGN

The conceptual design of the sulfur dioxide removal process presented herein is based on an integration of the system with one of the existing 60 Mwe generating units at the Watts Bar Station of the Tennessee

Valley Authority. Process and equipment designs were prepared in general on the same basis as the small pilot plant, which is described in Part VI of this summary report. The flow system, however, was redesigned. A single pump taking suction from the absorber supplies the entire head, and replaces the three pumps utilized in the small pilot plant. The additional pumps are required in the small pilot plant to provide the flow flexibility that will establish optimum operating conditions for subsequent plants. It is probable that further improvements in the design will be effected as more information becomes available from the experimental work in progress, and from subsequent small pilot plant operation. The design basis for the major components is given below.

1. Reducer

The reducer was designed for a three-hour hold up time, utilizing three stirred reactor tanks in series. Present studies may indicate that a perforated plate column or other countercurrent contactor should be substituted for the stirred reaction vessels. This would lead to substantial savings, according to estimates made for the small pilot plant components described in Part VI of the summary report. Since utilization of columns will be determined after the small pilot plant tests are analyzed, this report is based on the more expensive (and thus more conservative) assumption that stirred reactor vessels will be used.

The reactor vessel size is based on a reaction time requirement of one hour and an equivalent 3 to 1 recirculation rate in order to provide excess sulfide. The provision of the additional reducer capacity eliminates the recirculation pump utilized in the small pilot plant. Future investigations may show that all or most of the additional hold up time to

provide excess sulfide will not be necessary. If so, only one-third of the tank capacity will be needed.

2. Regenerator

The regenerator was designed for a one-hour hold up time, also utilizing three stirred reactor tanks in series. It is expected that the required reaction time will actually be considerably less than one hour, so a conservative tank capacity is provided.

It should be noted that a perforated plate column or other countercurrent contactor could be substituted for the stirred reactor vessels for this service also, if experimental results indicate.

3. Heater

The electric heater upstream of the reduction step is designed to heat the melt stream at full load from 800°F to 1100°F in 8 hours. A regenerative heat exchanger will also be employed in the process, reducing the steady state requirements on the electric heater to approximately 10% of those required during startup.

4. Reducing Gas Generator

The reducing gas generator was sized to produce 125% of the theoretical requirement. The plant cost was based on producing a hydrogen-rich gas containing approximately 10% carbon monoxide and 12% carbon dioxide; or alternatively, 25% carbon monoxide and no carbon dioxide. The plant can also be furnished with a 96%+ hydrogen mixture at approximately 40% higher gas generator cost.

5. Electrostatic Precipitator

The electrostatic precipitator was sized and priced to remove 99.9% of the fly ash. This high efficiency will not be required if it

becomes possible to recover the salt from the fly ash filter cake economically, or when a low cost liquid spray is used to remove fly ash prior to the absorption step. However, a high efficiency electrostatic precipitator must be included until better methods to prevent fly ash interference are developed. The premium for the high efficiency precipitator thus offers an incentive to develop alternate methods of handling the problem of fly ash removal and salt recovery.

6. Fly Ash Filter

Two fly ash filters are provided prior to the reduction step, each sized for a one-day loading cycle before cake removal and on the basis that the electrostatic precipitator has only a 99% efficiency. This will allow some flexibility in the operation of the filters and precipitator.

7. Absorber

The absorber has been designed as a spray column with a flue gas velocity of 25 ft per second at 800°F.

8. Pump

The system was designed for continuous flow. A pump in the coldest portion of the process system provides the entire head required.

B. PROCESS DESCRIPTION

1. Flue Gas Stream

Flue gas is drawn from the existing boiler at 800°F and ducted to the electrostatic precipitator. The gases are then routed to the absorber and ducted back into the boiler for further heat rejection in the air heater. The flue gas throughput at full load will be 422,000 cubic feet per minute at 800°F. The most convenient place to extract the flue gases at the Watts Bar installation is just downstream of the economizer. It is

estimated that the temperature there is approximately 700°F, necessitating a bypassing and mixing of hotter gases from the preceding boiler pass to bring the total flue gas to the desired temperature level. At full load 26 tons of coal containing an estimated 1560 pounds of sulfur are fired per hour. The electrostatic precipitator was sized on the basis that the ash content in the coal is 10%, that at least 90% of the ash will turn into fly ash, and that 99.9% of the fly ash is removed by the precipitate.

After leaving the precipitator, the gas stream is passed through an open spray tank scrubber where it is contacted with sprays of molten carbonate at 800°F. All of this will cause an additional pressure loss in the gas stream of less than 3 in. of water. The existing blower is apparently sufficiently oversized to be able to accommodate the additional load. Table 1 lists the flue gas stream equipment required, and its size.

TABLE 1

GAS STREAM EQUIPMENT REQUIRED

| Item | Size (ft.) |
|---|---|
| By-pass duct for reheating | 25 x 1 |
| Transfer duct to and from boiler economizer section | 30 x 30 |
| Main ducting to and from electrostatic precipitator | 14 x 10 |
| Electrostatic precipitator | 52 W x 39 D x 34 H |
| Electrostatic precipitator headroom | 57 |
| Absorber | 17 x 17 x 25 high |

2. Process Stream

The large pilot plant process flow diagram is shown in Figure 1. A molten carbonate flow of 20,000 lb per hour is sprayed into the scrubber. A liquid-level controller at the bottom of the absorption tank regulates the makeup to the system, by holding the liquid inventory in the system constant. A flow indicator controller in the line between the absorber and pump regulates a control valve to assure constant flow of liquid. Two pumps, each sized for the total duty, are located in parallel to increase the reliability and maintainability of the system. The use of one pump at the lower temperature to develop the entire system head eliminates the need for a high temperature pump. The pump takes suction from the absorber at a temperature of 800°F. If a pump were also required to take suction from the reducer, the pump design temperature would be above 1100°F. The pumps are designed to deliver 150 psi pressure, which is dissipated in the subsequent equipment.

The fly ash not removed in the electrostatic precipitator will be removed from the gas stream by the carbonate in the absorber, and will be filtered out ahead of the reduction step. Two filters are provided in parallel for continuous operation. Due to the porosity of the fly ash, approximately 50% of the total volume of the filter cake will be melt. After filtration, the liquid stream passes through a regenerative heat exchanger and then past an immersion heater, where the melt temperature is raised to the desired 1100°F level for the reduction step. The flow then enters three stirred tank reducers placed in series, each equipped with a liquid level controller and valving to provide a continuous flow and constant holdup time. Reducing gas is generated on site, in a packaged low pressure gas-steam reformer, and fed into the reaction vessels. Although

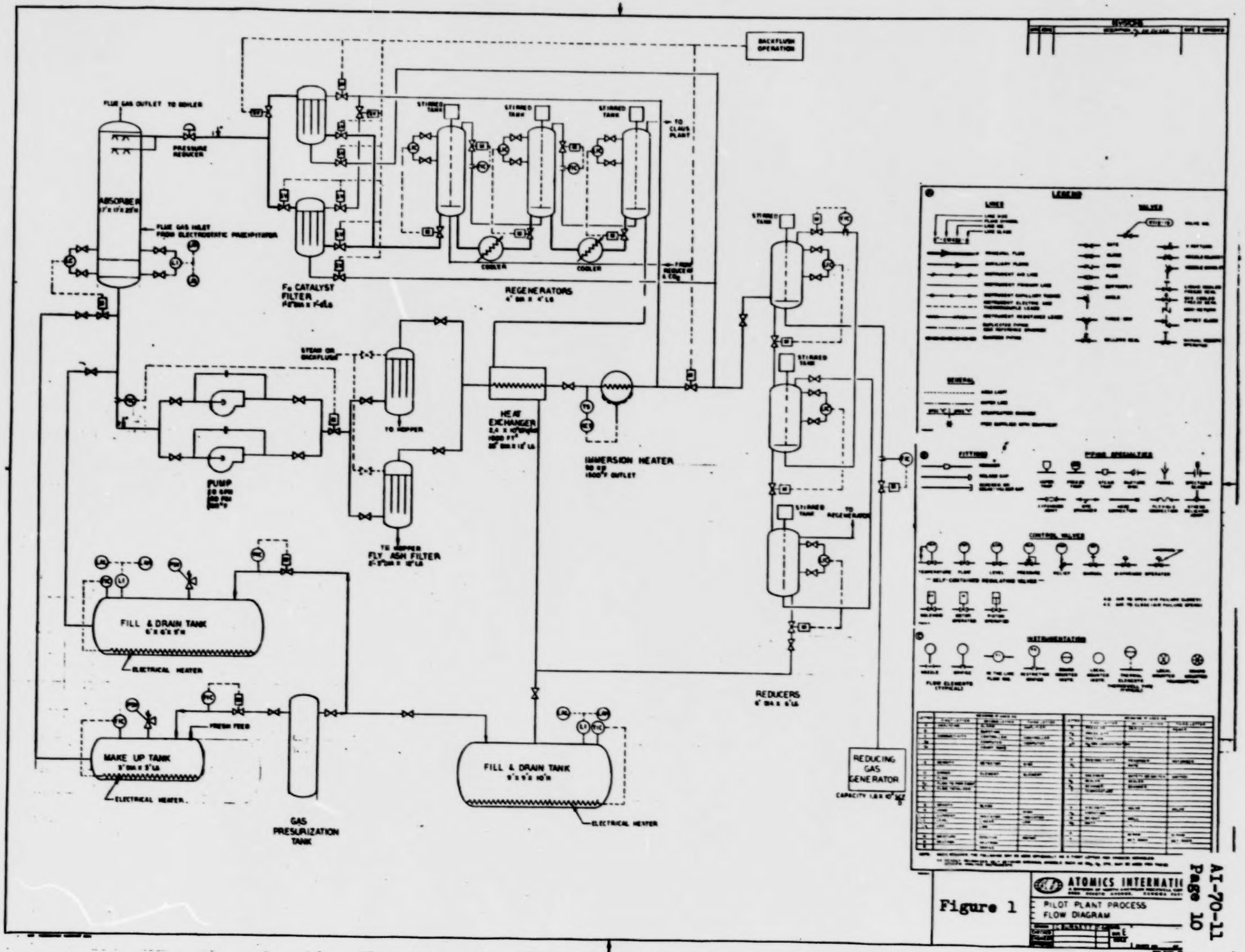

BACKFLUSH OPERATION
FLUE GAS OUTLET TO BOILER
PRESSURE REDUCER
ABSORBER
FLUE GAS INLET FROM ELECTROSTATIC PRECIPITATOR
Fe CATALYST FILTER
REGENERATORS
STIRRED TANK
COOLER
TO CLAUS PLANT
STEAM OR BACKFLUSH
PUMP
TO HOPPER
FLY ASH FILTER
HEAT EXCHANGER
IMMERSION HEATER
REDUCERS
FILL & DRAIN TANK
ELECTRICAL HEATER
MAKE UP TANK
FRESH FEED
GAS PRESURIZATION TANK
REDUCING GAS GENERATOR
LEGEND
LINES
VALVES
PIPING SPECIALTIES
CONTROL VALVES
INSTRUMENTATION
ATOMICS INTERNATIONAL
PILOT PLANT PROCESS FLOW DIAGRAM

Figure 1

the flow diagram shows the gas flow co-current with the liquid stream, countercurrent flow is also possible.

The reduced melt is then cooled to 850°F in the regenerative heat exchanger before it enters the regenerator. The regenerator shown consists of three stirred reaction vessels in series, with intercoolers to remove the heat produced by the exothermic regeneration reaction. Present studies may indicate that a perforated plate column or other countercurrent contactor should be substituted for the stirred reaction vessel. The pilot plant analysis shows a reduction in cost when a column is substituted for a stirred reaction vessel. The intercooling will be controlled by utilizing an intermediate stream (perhaps Dowtherm) before final heat rejection. Level indicator controllers on each vessel assure constant flow and holdup time. The exit gas from the reducer, and additional carbon dioxide, if required, is passed countercurrent through the regenerator. Iron oxide catalyst utilized in the reducer is filtered downstream of the regenerator. Two iron catalyst filters are utilized. A backflush operation allows fluid from the 1100°F heater to wash out the accumulated catalyst and return it to the reducer. The molten carbonate passing through the filter is returned to the absorber. The system is pressurized to 150 psi, mainly to supply approximately 120 psi pressure at the reducer to speed the reaction. Since pressure apparently provides no advantage in the regeneration step, the pressure reducer shown ahead of the absorber will be relocated ahead of the regenerator. Sufficient head will, of course, be allowed for the pressure drop of the liquid and gas downstream of the pressure reducer.

The entire system will be drainable into the fill and drain tanks provided. All equipment, piping, etc. containing molten carbonate

will be provided with electric heating elements and insulation. Table 2 lists the major process equipment items and their sizes.

TABLE 2

EQUIPMENT REQUIRED

| Item | Size |
|---|---|
| Molten Carbonate Lines | 1½" Sch 10 |
| Pumps (2) | 20 GPM |
| Fly Ash Filters (2) | 2'3" Diam x 12' L |
| Salt-to-Salt Heat Exchanger | 1000 $ft^2$<br>26" Diam x 12' L |
| Immersion Heater | 90 kw |
| Reducers (3) | 6' Diam x 6' High |
| Regenerators (3) | 4' Diam x 4' High |
| Regenerator Coolers (2) | 1'2" Diam x 6' L |
| Fill and Drain Tank (Absorber Capacity) | 6' x 6' x 5' |
| Make-up Tank | 3' Diam x 3' L |
| Fill and Drain Tank (Process System) | 9' x 9' x 10' |

A rough layout of the process equipment, not including the absorber or reducer gas plant, shows a plot requirement of 60 ft by 30 ft. The reducer gas plant was estimated by the C. I. Girdler Corp. to require a plot of 71 ft by 24 ft.

The reducer, heater, and regenerative heat exchanger will be made of a special high temperature alloy such as Hastelloy G or Uniloy; the other equipment in contact with the melt, such as the scrubber, will be made of type 347 stainless steel.

C. INTEGRATION

Several TVA installations were visited during the contract period to assess the feasibility of adapting the molten carbonate process into the respective power plants. The plants visited were the Bull Run Power Plant, the Kingston Power Plant and the Watts Bar Power Plant. At each location, the following major areas of concern were investigated:

(1) Space. The layout of the power plant and the space availability.

(2) Thermal. The thermal distribution within the boiler and the accessibility of the proper zone to gas treatment ducting. Also, the temperature variation with load.

(3) Hydraulics. The draft system characteristics and the available pressure drop.

(4) Impurities. The fly ash removal and handling problems.

It is believed possible to integrate the large pilot plant into any one of the three plants visited. It was concluded that use of the Bull Run Plant is probably precluded because it is very large (900 Mwe) and the cost of shutting down the plant for the modifications required would be very high. Of the remaining two plants, the Kingston #9 boiler would probably be easier from a spatial point of view, while the Watts Bar Plant is more likely to be available for modifications. For the purpose of the conceptual design, an integration with the Watts Bar Power Plant was chosen.

There are four boiler units at Watts Bar, each rated at 60 Mwe. The boiler must be modified to allow bypass of hot gases to mix with the gases presently leaving the boiler section at 700°F. A cursory look found

this to be feasible, but it will most likely result in a slight decrease in overall boiler efficiency. However, this should not be too important, since operation of the boilers at Watts Bar is not predicated on their efficiency. A breeching in the boiler is contemplated, to carry the gases from the boiler outlet through an opening in the boiler room wall north (into the present parking area) and into the electrostatic precipitator. Although it may be possible to locate the electrostatic precipitator and absorber in the boiler building, the estimate is based on locating the equipment outside of the building. Two factors led to this choice. The assembly of the large precipitator and absorber inside of the building would be costly and difficult, and equipment now located in the required space would have to be relocated, resulting in crowded conditions.

D. COST ESTIMATE

A budgetary estimate of the capital costs was prepared. Budgetary prices were received from vendors for the electrostatic precipitator, fly ash filter and reducing gas generator. The cost for the Claus Plant to convert the gases leaving the regenerator into elemental sulfur was estimated by A. M. Kinney, Inc., as stated in their final report (Task Order No. 1, Contract No. PH-86-68-92). This estimate was incorporated after adding the contractor's overhead plus a 20% contingency. Table 3 is a cost estimate breakdown of the process components, including modifications to the flue gas ducting of the power plant.

The cost to fill the system with molten carbonate has been estimated at $25,000.

TABLE 3

PROCESS EQUIPMENT COST ESTIMATE BREAKDOWN

| | |
|---|---|
| 1 Electrostatic Precipitator | $ 400,000 |
| 1 Absorber Tank | 90,000 |
| 1 Sump Tank for Absorber | 2,500 |
| 1 $CO_2$ System | 3,500 |
| 2 Pumps 20 GPM 4 P150# T850° | 50,000 |
| 1 Back Flush System for Filters | 8,000 |
| 2 Fly Ash Filters | 108,000 |
| 1 Heat Exchanger Salt-to-Salt | 62,000 |
| 1 Heater 90 kw - Immersion Type | 56,500 |
| 3 Tanks Agitated @ 1150°F - Reducer | 152,000 |
| 1 Reducing Gas Generator | 330,000 |
| 2 Fe Catalyst Filters | 19,000 |
| 3 Tanks Agitated @ 850°F - Regenerator | 51,000 |
| Piping and Fittings | 14,300 |
| 2 Regenerative Coolers | 20,200 |
| Valves and Operators | 80,800 |
| Flue Ducting and Plant Modification | 101,400 |
| Precipitator - Inlet and Outlet Transition | 23,300 |
| Pad and Chemical Structure | 36,000 |
| Make-up Tank | 1,300 |
| Fill and Drain System | 3,600 |
| Instrumentation | 157,000 |
| Electrical (including Preheat) | 34,600 |
| Sampling Station | 400 |

TABLE 3 (cont'd)

| | |
|---|---|
| Precipitator Foundations | 7,000 |
| Insulation | 38,500 |
| Fly Ash Handling (Disposal) System | 15,000 |
| Contractor's Overhead and Profit Plus 20% Contingency | 824,100 |
| Subtotal | $2,700,000 |
| Claus Plant | 510,000 |
| Total | $3,210,000 |

The operating costs for the plant have been estimated at approximately $150,000 per year. The reducing gas cost contributes $114,000 per year, on the basis of producing the gas at 21¢ per 1000 SCF and a plant factor of 90%. The carbonate make-up contributes $6,400 per year, on the basis of no recovery of carbonate from the fly ash filter cake, a 99.9% electrostatic precipitator efficiency, and a cost of 22¢ per pound for the mixed carbonates.

## III. SYSTEM DESCRIPTION OF A FULL SIZE PLANT (800 Mwe)

### A. BASIS OF DESIGN

The conceptual design of a prototype full size plant was based on integrating the process into an 800 Mwe power plant. The power plant was conjectured to be in the planning stage, so the power plant design could therefore be optimized to allow for the integration of the sulfur dioxide removal process. The full size prototype plant design will be based on the prior operating results from the small pilot plant, the component test loop, and the design effort of the large pilot plant. The conceptual design

presented is therefore preliminary, and devoted primarily to estimating the capital and operating costs of the process. This makes it possible to recognize the important cost contributions and to guide further development effort toward reducing the overall costs to a minimum. The conceptual design presented is essentially based on the expanded requirements of the large pilot plant and, to provide a common comparative cost base, in part on the assumptions and cost data presented in the work by S. Katell.[1] The design basis for the major components follows.

1. Reducer

The reduction step is based on utilizing hydrogen or a reformer gas mixture as the reducing agent. Plant analysis shows that the overall cost can be materially reduced when carbon or the gases from a steam-coal reaction are utilized. It should therefore be recognized that although this estimate based on hydrogen as a reducing agent is representative of the technology developed thus far, the estimate is probably very conservative.

The reducer was designed for a one-hour reaction time. Three stirred reaction tanks are provided in series. Disproportionation of the sulfite in the heat exchanger prior to the reduction step should provide all the required initial sulfide (about 8%), and thus eliminate the need for recirculation.

As was noted in Section II A for the large pilot plant, present studies may indicate that a perforated plate column or other countercurrent contractor should be substituted for the stirred reaction vessels. This would lead to substantial savings, according to estimates made for the small pilot plant components described in Part VI of the summary report. Since

utilization of columns will be determined after the small pilot plant tests are analyzed, this report is based on the more expensive (and thus more conservative) assumption that stirred reactor vessels will be used.

2. Regenerator

The regenerator was designed for a 20-minute hold-up time, also utilizing three stirred reactor tanks in series. The comments on substitution of a column for the stirred reactor tanks also apply here.

3. Reducing Gas Generator

The reducing gas generator was sized to produce 125% of the theoretical requirement. Costs were obtained for both high purity hydrogen (96+%) and a 71% hydrogen-25% carbon monoxide mixture.

4. Electrostatic Precipitator

Although it is recognized that the final version may employ a molten salt recovery system, this conceptual design is based on utilizing a 99.9% efficient electrostatic precipitator and disposing of the fly ash-salt mixture filtered from the liquid stream.

5. Fly Ash Filter

Two fly ash filters are provided prior to the reduction step, each sized for one day of operation between cake removal cycles.

6. Absorber

The absorbers have been designed as spray columns, with a flue gas velocity of 25 ft per sec.

7. Pump

The system was designed for continuous flow. A pump taking suction from the absorber provides the entire head required.

B. PROCESS DESCRIPTION

1. Flue Gas Stream

The layout of the boiler will allow flue gases to be drawn from the 800 to 850°F zone and ducted to an electrostatic precipitator. From the outlet of the precipitator the gases are ducted to the absorber and then back to the boiler for further heat rejection in the economizer zone and air heater. The flue gas throughput at full load will be 88 x $10^6$ standard cubic ft per hour. At full load 280 tons per hour of coal are consumed, containing an estimated 16,800 pounds per hour of sulfur. The electrostatic precipitator was sized on the basis that the ash content in the coal is 10%, at least 90% of the ash becomes fly ash, and 99.9% of the fly ash is removed. The penalties associated with this high efficiency and possible alternatives are treated further in Section IV, Plant Analysis Studies. The flue gases from the precipitator are then passed in parallel through five spray scrubbers where they are contacted with molten carbonate at 800°F. The pressure loss in the gas stream, estimated at less than 3 in. of water, is provided by the blower in the flue gas system. Table 4 lists size and material of construction of the precipitator and absorbers.

TABLE 4

FLUE GAS EQUIPMENT REQUIRED

| Item | Size | Material |
|---|---|---|
| Electrostatic Precipitator | 222' wide 42' deep 35' high | Carbon Steel |
| Absorber (5) | 25' diam 20' high | SS Type 347 |

2. Process Stream

The process flow diagram is shown in Figure 2. A molten carbonate flow of 150,000 lb per hour is sprayed into the absorbers. A liquid level controller at the bottom of the absorption tank regulates the makeup to the system by holding the liquid inventory in the system constant. A flow indicator controller in the line between the absorber and pump regulates a control valve to assure constant flow of liquid. At the outlet of the absorber 30% of the melt is in the form of sulfite and sulfate. The flow rates of the process stream are shown on the flow diagram.

Two free-surface centrifugal type pumps, each sized for the total duty of approximately 160 gal. per minute, are designed to deliver 150 psi head which is dissipated in the subsequent equipment. The reducer pressure will be lowered to about 120 psi by pressure loss in the filter, heat exchanger and heater. Since the reaction rate in the regenerator is not enhanced by pressure, a pressure reducing valve will be located between the reducer and regenerator to control the head at the regenerator to allow only for the required pressure losses downstream of the regenerator.

Two filters are provided in parallel for continuous filtration of the fly ash removed in the absorption step. The filter cake contains approximately an equal amount of liquid and ash, due to the 50% porosity of the ash. Although the costs presented are based on a 99.9% efficient electrostatic precipitator which minimizes the quantity of molten carbonate lost, present efforts on economic recovery of the salt from the cake may alter this requirement.

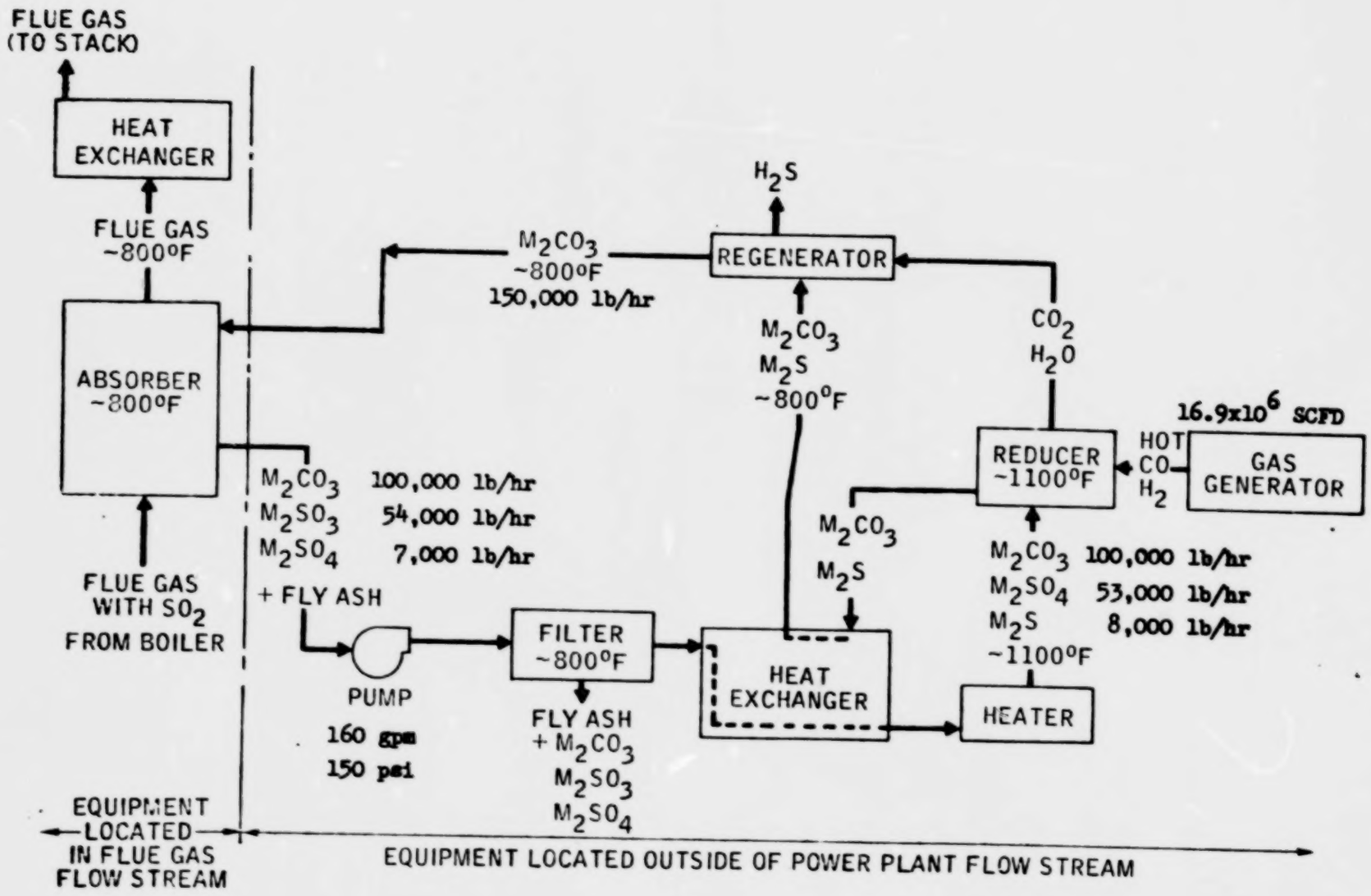



**Figure 2. Process Flow Diagram for 800 Mwe Plant**

The temperature must be increased to 1100°F to speed up the rate of the hydrogen reduction step. A shell and tube regenerative heat exchanger and a salt heater are provided for this. The heat exchangers are based on an overall heat transfer coefficient of 115 Btu/hr ft °F. The heater is sized for a 15 x $10^6$ Btu/hr maximum capacity. This will allow a full flow heat-up from 800°F to 1100°F in approximately 1 hour.

The reducer consists of three stirred reaction vessels in series, equipped with liquid level controllers and valving to provide a continuous flow and constant holdup time. Reducing gas is generated on site in a packaged low pressure gas-steam reformer, and fed into the reaction vessel. The reduction step is a major contributor to the overall cost of the plant. Costs associated with alternate reducing agents are discussed further in Section IV, Plant Analysis Studies.

The reduced melt is cooled to 850°F in the regenerative heat exchanger, before it enters the regenerator. The regenerator also consists of three stirred reaction vessels in series, with intercoolers to remove the heat produced by the exothermic regeneration reaction. The type of vessel used may be altered if better performance can be attained by plate columns or others under study. Level indicator controllers on each vessel assure constant flow and holdup time. The exit gas from the reducer, and additional carbon dioxide if required, is fed countercurrently through the regenerator. The iron oxide catalyst utilized in the reducer is filtered downstream of the regenerator, using two iron catalyst filters in parallel. A backflush operation allows fluid from the 1100°F heater to wash out the accumulated catalyst and return it to the reducer.

The entire system will be drainable into the fill and drain tanks provided. All melt-containing equipment will be provided with electrical heating elements and insulation.

The reducer, heater and regenerative heat exchanger will be made of a special high temperature alloy such as Hastelloy G or Uniloy; all other equipment in contact with molten carbonate will be made of type 347 stainless steel.

Table 5 lists the major process equipment items and their sizes.

TABLE 5

EQUIPMENT REQUIRED

| Item | Size |
|---|---|
| Molten Carbonate Lines | 4" Sch 10 |
| Pump | 160 GPM |
| Salt-to-Salt Heat Exchanger Surface Area | 2500 $ft^2$ |
| Salt Heater | 15 x $10^6$ Btu/hr |
| Fly Ash Filters | 2'5" diam x 12' L |
| Reducers (3) | 8'6" diam x 10' H |
| Regenerators (3) | 6'3" diam x 8' H |
| Drain and Fill Tanks | 3500 $ft^3$ |
| Makeup Tank | 50 $ft^3$ |

C. INTEGRATION

At this stage of development, efforts are concentrated on a fit-up of the process with large power plants now in the planning stage. This makes it possible to optimize the system performance. It is interesting to note

the recent interest in hot flue gas electrostatic precipitation, which is a major integration requirement for the molten carbonate process. One large installation, the Ravenswood Plant of the Consolidated Edison Co., is operating a precipitator successfully at 700°F. Their reasons for adapting the high temperature precipitator are as follows:

(1) High collection efficiency with low sulfur coals (tests show greater than 99% efficiency).

(2) Possible collection and conveying of oil ash as well as fly ash.

(3) Less fouling of the air preheater.

In principle, the process precipitator requirements could be met by the Ravenswood design. The flue gas temperature would have to be raised by 100 to 200°F, which may necessitate rearrangement of the economizer to remove additional heat prior to the air preheater.

D. COST ESTIMATE

Operating and capital costs of the process for an 800 Mwe power plant were estimated. The basic assumptions in the cost evaluation were similar to those utilized by S. Katell[1] of the Bureau of Mines, in his economic comparison of sulfur dioxide removal processes. However, in order to assess the costs presented, the following differences in the assumptions should be noted:

(1) A high temperature electrostatic precipitator penalty cost to remove 99.9% of the fly ash was included in the component cost; in previous estimates the cost was based on a 95% fly ash removal. The referenced comparison (by Katell) did not include any fly ash cost penalties.

(2) The reducing gas used is obtained from a natural gas reformer. Previous cost estimates, as well as the referenced comparison, were based on a coal-steam producer gas generation.

(3) An 80% utilization of the reducing gas was used in all calculations. The referenced comparison assumes an 86% utilization.

(4) The equipment costs presented include a 20% contingency and 25% contractor's overhead. The referenced comparison does not state these items.

(5) The working capital was included at 6.5% of the total plant cost. The working capital in the referenced comparison varies from 2.8% to 6.6%.

The sulfur plant costs were estimated from the costs of similar plants for the Alkalized Alumina process referenced above. The costs for the natural gas reformer (hydrogen) plant, fly ash filters and electrostatic precipitator were based on budgetary prices from vendors. Estimates were based on using both 96%+ hydrogen gas and a 75%/21% hydrogen/carbon monoxide mixture as the reducing gas. A 20% contingency was added to the process equipment. The high temperature precipitator penalty was based on a differential cost that used a 99% efficiency unit handling 320°F flue gas as a base requirement.

Table 6 is a cost estimate breakdown of the process components.

TABLE 6

SUMMARY OF PROCESS COMPONENT COSTS FOR THE MOLTEN CARBONATE PROCESS ($10^3$ $)

| Major Components | Costs ($H_2$ Red'n) | Costs * ($H_2$/CO Red'n) |
|---|---|---|
| Absorbers | 400 | 400 |
| Reducers | 525 | 625 |
| Regenerators | 100 | 100 |
| Pumps | 100 | 100 |
| Salt Heater | 120 | 120 |
| Heat Exchanger | 75 | 75 |
| Makeup Tank | 10 | 10 |
| Storage Tank | 25 | 25 |
| Fly Ash Filter | 100 | 100 |
| | 1,455 | 1,555 |
| Instrumentation | 150 | 150 |
| Piping, Insulation Auxiliaries, etc. | 250 | 250 |
| | 1,855 | 1,955 |
| 20% Contingency | 371 | 391 |
| Hi Temp Precipitator Penalty | 3,000 | 3,000 |
| Total Absorber-Regenerator Cost | 5,226 | 5,346 |

* Based on reduction with a mixture of 75% $H_2$, 21% CO.

The investment cost of the process is summarized in Table 7, and the annual costs in Table 8. Table 7 shows total plant investments of $11,228,000 and $11,686,000. Both include a high temperature electrostatic precipitator penalty of $3,000,000. These costs are believed to be conservative. There is an incentive to recover molten carbonate from fly ash to reduce the precipitator requirement, and there is an incentive to eliminate the hydrogen generator by using carbon as the reducing agent. (See page 47 for the reduction associated with use of carbon). Table 8 shows the net operating cost to be 0.622 mils/kwh for a 96%+ hydrogen gas and 0.56 mils/kwh for a 75/21 hydrogen/carbon monoxide mixture. Further verification of the assumed reaction rates will determine the optimum composition. First estimates (see Section IV, Plant Analysis) show that this cost can be reduced materially utilizing fluidized coke as the reducing agent.

The costs presented do not include sulfur credit, flue gas stack height reduction credit, or corrosion reduction credit. In the analysis of the Dolemite process, Combustion Engineering reported that a credit of $1.12 per installed kilowatt is possible when the stack height is reduced from 800 to 300 ft. For an 800 Mwe plant this amounts to $895,000 in capital equipment. They also estimated that elimination of sulfur dioxide will reduce corrosion, and credit 5.3¢ per ton of coal fired. This would allow a credit of 132,500 per year. These two items would reduce the net operating cost 0.04 mils/kwh.

The plant can produce 63,200 tons of sulfur per year. Based on a selling price of $40 per ton, $2,530,000 in revenue per year can be realized. This is the equivalent of a cost reduction of 0.40 mil/kwh. These credits will materially reduce the actual cost of removing the sulfur dioxide from the plant flue gas.

TABLE 7

TOTAL ESTIMATED CAPITAL REQUIREMENTS ($10^3$ $)

| Item | Costs ($H_2$ Red'n) | Costs ($H_2$/CO Red'n) |
|---|---|---|
| Absorber-Regenerator | 5,226 | 5,346 |
| Coke Handling | | |
| Reduction Gas Producer | 2,500 | 2,000 |
| Sulfur Recovery | 1,780 | 1,780 |
| Plant Facilities | 470 | 460 |
| Plant Utilities | 665 | 640 |
| Total Construction | 10,641 | 10,226 |
| Initial Charge | 95 | 95 |
| Total Plant Cost | 10,736 | 10,321 |
| Interest During Construction | 255 | 247 |
| Subtotal for Depreciation | 10,991 | 10,568 |
| Working Capital | 695 | 660 |
| Total Investment | 11,686 | 11,228 |

TABLE 8

ESTIMATED ANNUAL AND NET OPERATING COSTS*
($10^3$ $)

| Item | Costs ($H_2$ Red'n) | Costs ($H_2$/CO Red'n) |
|---|---|---|
| Direct Cost | | |
| Raw Materials and Utilities | | |
| Absorbent | 83 | 83 |
| Reducing Agent | 1,290 | 975 |
| Power Water Heat | 158 | 158 |
| Subtotal | 1,531 | 1,216 |
| Direct Labor | | |
| 72 mh/day x 2.75/mh | 83 | 83 |
| Plant Maintenance (3% of Depreciation Base) | 328 | 315 |
| Payroll Overhead (18.5% of Payroll) | 63 | 61 |
| Operating Supplies (20% of Plant Maint.) | 65 | 63 |
| Total Direct Cost | 2,070 | 1,738 |
| Indirect Cost (50% Labor, Maint. and Supplies) | 238 | 230 |
| Total Capital Charges (14% of Total Invest.) | 1,632 | 1,570 |
| Net Operating Cost | 3,940 | 3,538 |
| Net Operating Cost (mils/kwh) | 0.622 | 0.56 |

*No sulfur credit, flue gas stack reduction credit, or corrosion reduction credit

# IV. PLANT ANALYSIS STUDIES

## A. INTEGRATION CONSIDERATIONS

A conceptual study is being conducted to evaluate the problems associated with integrating the molten carbonate process into commercial power plants. To date, only preliminary analysis and problem definition has been accomplished. Four main integration considerations have been identified. These are space, thermal, hydraulic and impurity effects.

### 1. Space Considerations

There are four major items in this category:

a) The available locations to place the required equipment must be ascertained.

b) The various possible process component configurations must be laid out.

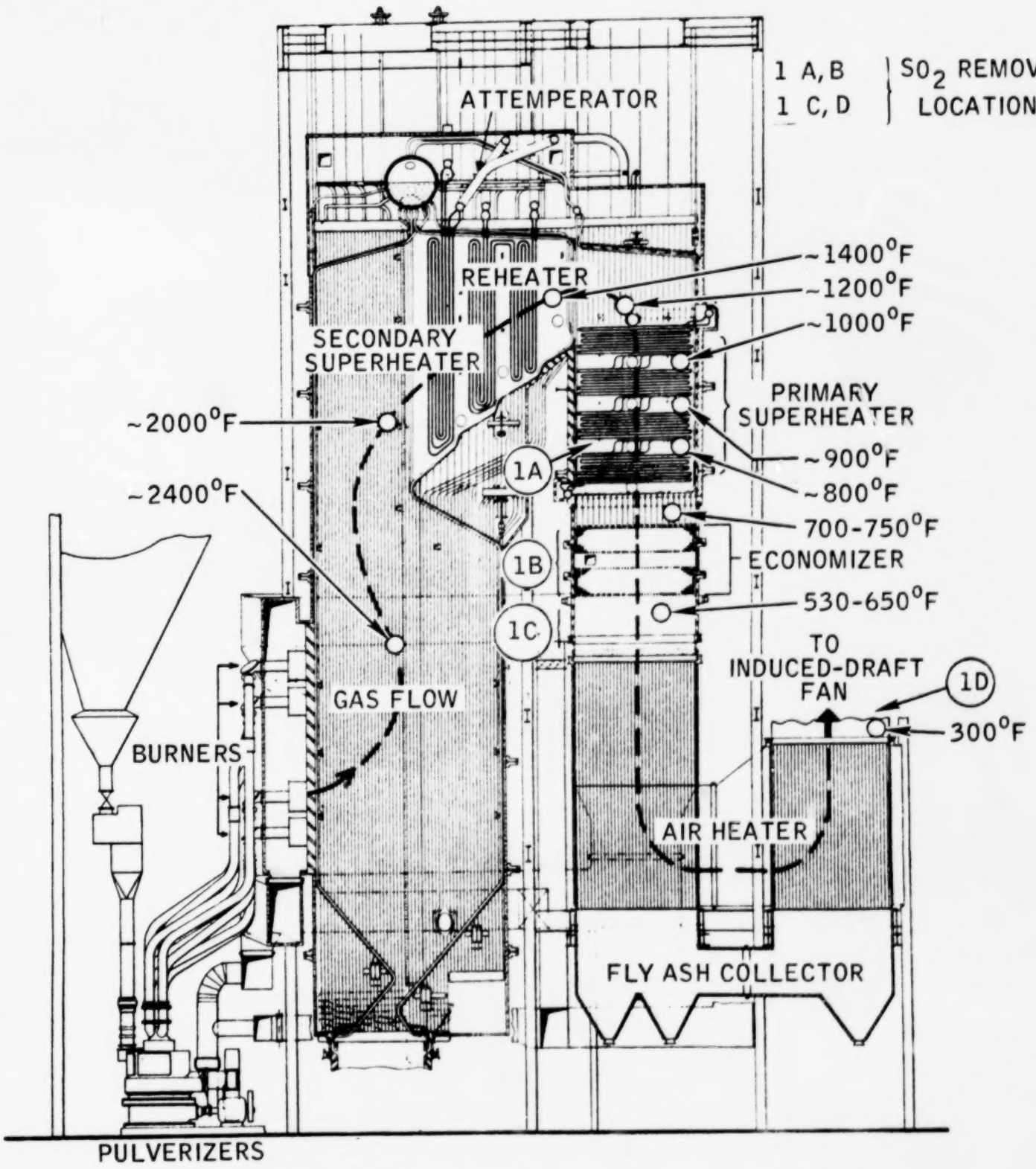
c) The possible boiler plant component rearrangements must be evaluated.

d) The fit up requirements must be evaluated.

Figure 3 shows a cross section of a large radiant boiler. Although typical, it is only one of many types and configurations. Boilers are custom designed because (1) steam requirements are so varied, (2) there are so many different kinds and grades of fuel, and (3) there are many design features possible to optimize the system. Real estate is usually expensive, and therefore the layout of the power plant can be expected to pose space problems. The flue gas must be diverted from the boiler at a suitable location, ducted to a location that can accommodate the electrostatic precipitator and absorber, treated to remove the sulfur oxides, and ducted back to the boiler for further heat rejection.

Figure 3

# TYPICAL LARGE RADIANT BOILER



The flue gas flow in a 200 Mwe power plant, for instance, is 1,000,000 CFM at 800°F. The cross section of a duct when the velocity is held to 50 ft per sec is 17.3 ft by 17.3 ft. Final dimensions will of course, be based on a trade off with pressure losses, but are stated here only to show that sizeable openings in the boiler will be required.

2. Thermal Considerations

There are three major items in this category:

a) The boiler temperature distribution will determine a suitable location for diverting the flue gases for processing.

b) The temperature variation with load will determine the control requirements for part load operation.

c) The process stream temperature must be maintained to prevent freezing of the molten carbonate in the absorber.

A typical temperature distribution throughout the boiler is superimposed in Figure 3. These temperatures vary, of course, with boiler design; however, those shown are realistic and typical. Four possible locations for the outlet ducting of flue gases are identified in Figure 3. The gas temperature of 800°F, most desirable for gas treatment, usually occurs somewhat upstream of the economizer zone; the gases entering the economizer zone are generally around 750°F. Blending of bypassed flue gases from the hot zone could be utilized to raise this gas temperature. At the exit of the economizer the gas temperatures are about 650°F. If the outlet ducting is located in this zone, the flue gases must be reheated, and provisions made for subsequent recovery of the additional heat. It is also conceivable

to treat the gases after they leave the air heater. Since this would require considerable reheating, subsequent heat recovery would be essential.

The gas temperature at any point in the boiler will vary with the load. Since most electrical stations consist of multi-boiler installations, the load that each boiler supplies is set by optimizing the output from each boiler to the lowest overall cost for making the electricity. Demand varies during the day and during the seasons, and the molten carbonate system must be designed for these temperature variations. Figure 4 shows the temperature variation with load at five different locations for one plant. The temperature at the scrubber must be maintained, and will therefore require adjustments at lower loads for continuous operation. This can be accomplished by bypassing hot gases, reheating, or not processing the gases at a predetermined cutoff point.

3. Hydraulic Considerations

There are three major items in this category:

a) The increase of flue gas pressure drop must be determined.

b) The effect of configuration on pressure drop must be determined to arrive at an optimum condition.

c) The power plant must be designed to accommodate the changes.

To provide the additional draft requirement caused by the losses incurred in the ducting, electrostatic precipitator, and absorber, additional power must be provided. This can be accomplished by adding a booster fan prior to or after the scrubber, by increasing the capacity of the induced draft fan in a balanced draft system, or by increasing the capacity of the forced draft fan in a forced draft system. Figure 5 shows the

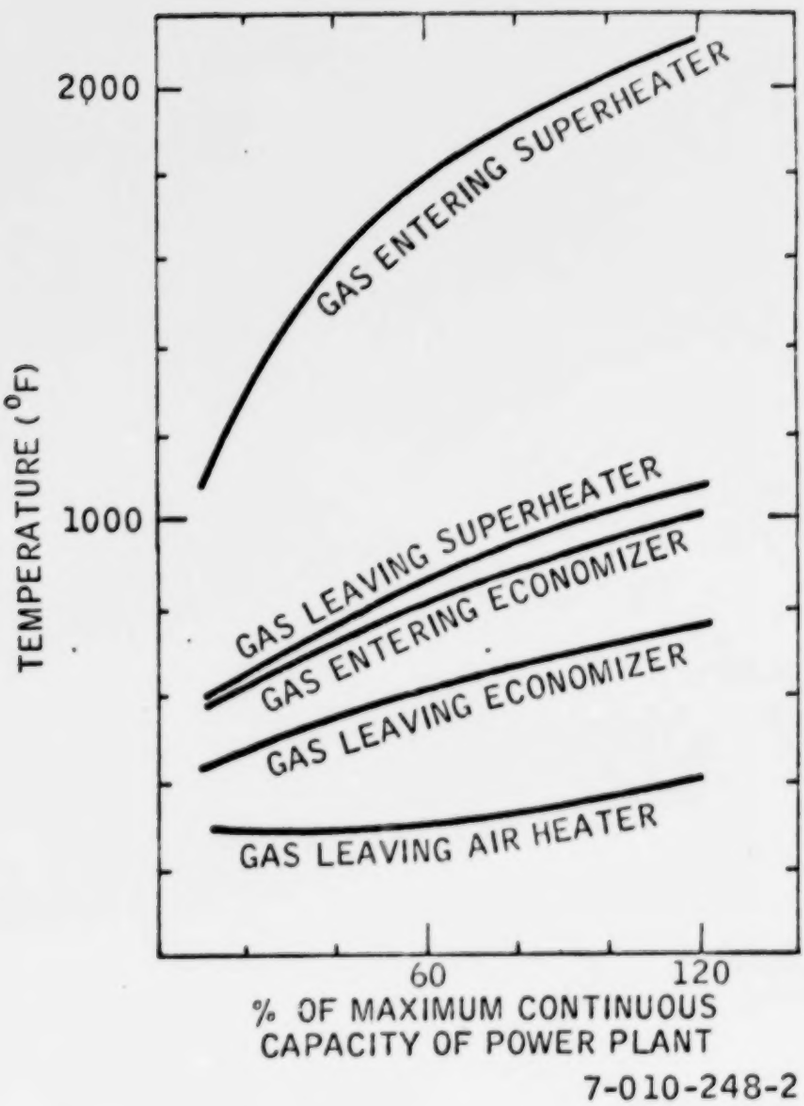



**Figure 4. Flue Gas Temperature**

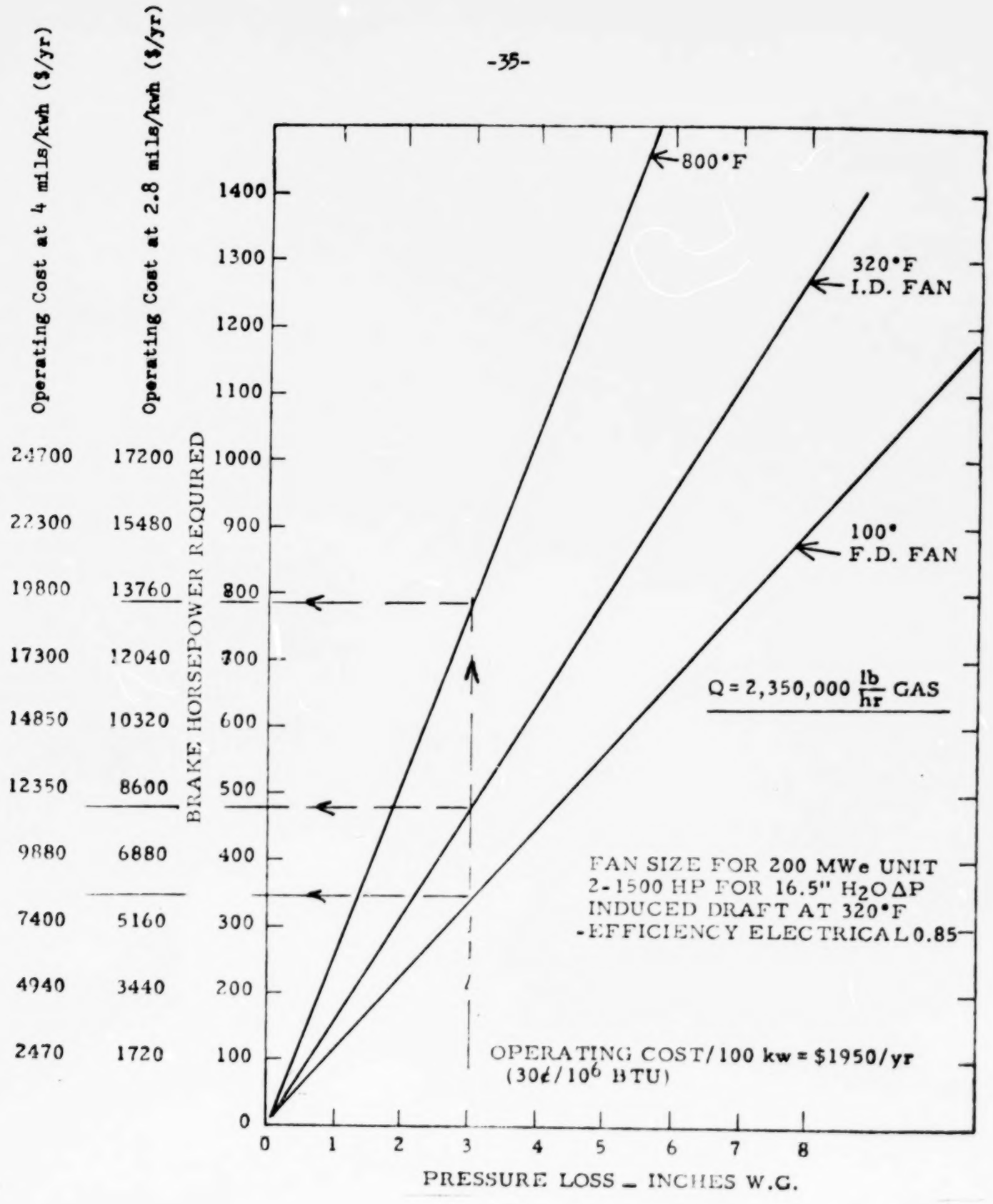



Figure 5. Horsepower Requirements as a Function of Pressure Drop for a 200 Mwe Power Plant

horsepower requirements for each of these methods as a function of pressure losses for a 200 Mwe power plant. The fan efficiency for the 100°F and 320°F cases was assumed to be 75%; however, at 800°F (per manufacturer's advice), the fan efficiency was reduced to 53%. For comparison it should be noted that an actual working plant this size contains two 1500 horsepower fans to produce the required induced draft. The parametric study shows that the pressure loss in the absorption column must be a major consideration in the design of the system. If the pressure losses can be kept below 3 in. of water, the existing draft fans can probably supply the additional requirements without the installation of a new fan. When a spray column is used as the absorber, the pressure loss will be less than 3 in. of water.

The operating costs of Figure 5 were calculated for power costs of 2.8 mils/kwh and 4 mils/kwh. The 2.8 mils/kwh reflect the fuel cost at $30¢/10^6$ Btu as the sole contribution to the power cost. The 4 mils/kwh reflects a typical total cost of producing power.

The total cost of the draft requirements is the sum of the operating and capital costs. For a balanced draft system of a 200 Mwe plant, the flue gas pumping costs were plotted as a function of pressure loss through the absorber in Figure 6. The step change in the induced draft fan cost occurred when the existing fan had to be replaced with a larger capacity unit. In all cases, the addition of a booster fan would result in a penalty over increasing the capacity of the induced draft fan. This same relationship will exist in a forced draft system. For a new power plant the step change due to replacement of equipment does not occur, and the cost curve will increase at the operating cost rate increase and a small incremental capital cost increase.

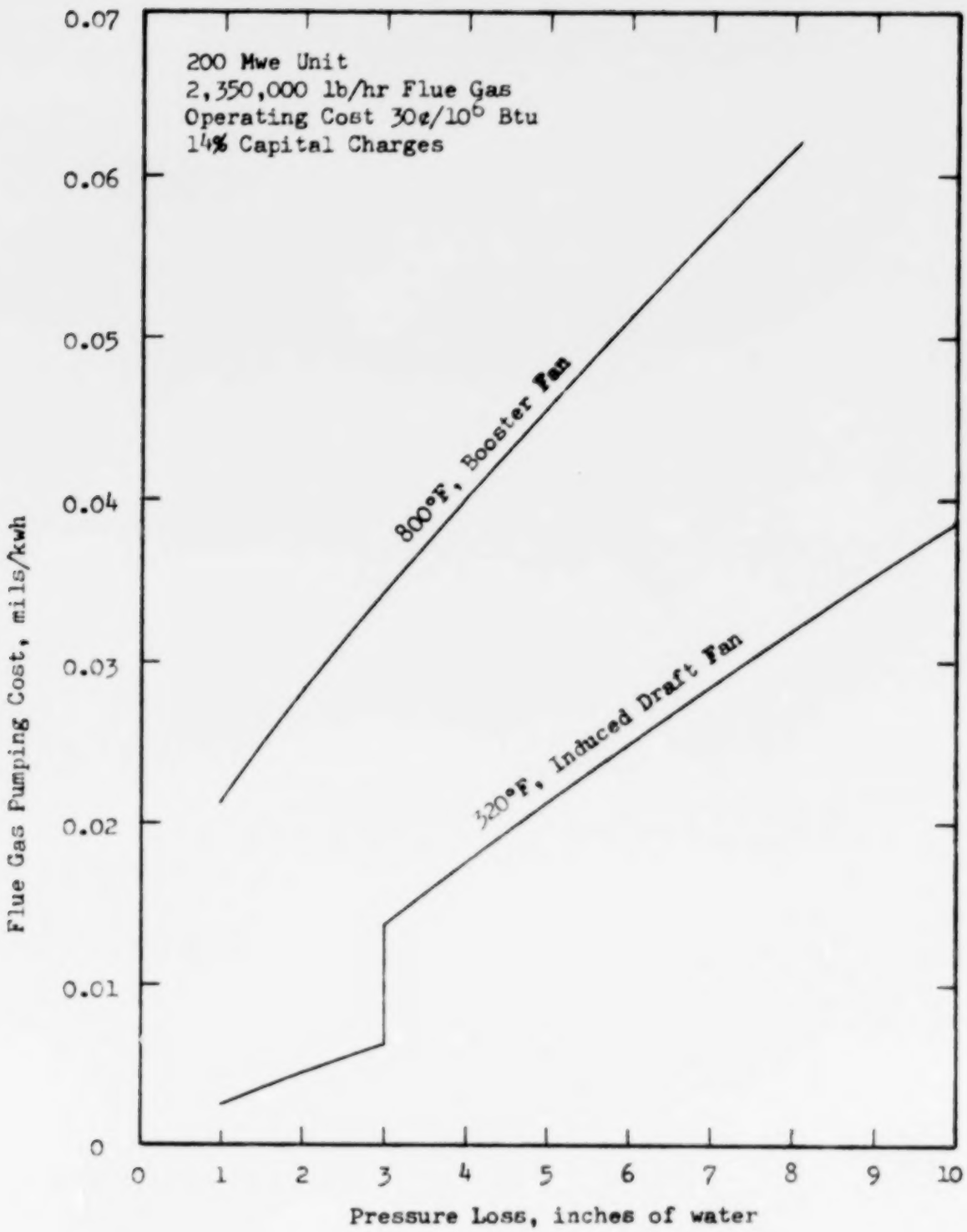



Figure 6. Cost of Draft Loss

4. Impurity Effects

There are two major items in this category:

a) The type and efficiency of the fly ash removal equipment.

b) The recovery of molten carbonate absorbed by the fly ash in the absorber and filtered out of the system.

An important consideration in the integration of the sulfur oxides removal process is the amount and characteristics of the fly ash contained in the flue gases. Figure 7 shows the distribution of the fly ash particle size for various coal firing methods. The percentage of ash contained in the coal that ends up in the flue gas is also listed in Figure 7, as a function of firing method.

An existing 200 Mwe station firing pulverized coal experiences a fly ash content of 4 grains per standard cubic foot of flue gas, leading to a fly ash quantity of 16,650 lb per hour at full load for the station.

Any quantity of fly ash not removed prior to contact with the molten carbonate will be removed by the carbonate spray. An equal quantity of molten carbonate will be contained in the fly ash filter cake removed from the process stream. (See Section C below).

Fly ash collection from the flue gas stream can be effected by the following principles:

a. Sudden velocity decrease

b. Change in flow direction

c. Impingement

d. Centrifugal force

e. Electrostatic field.

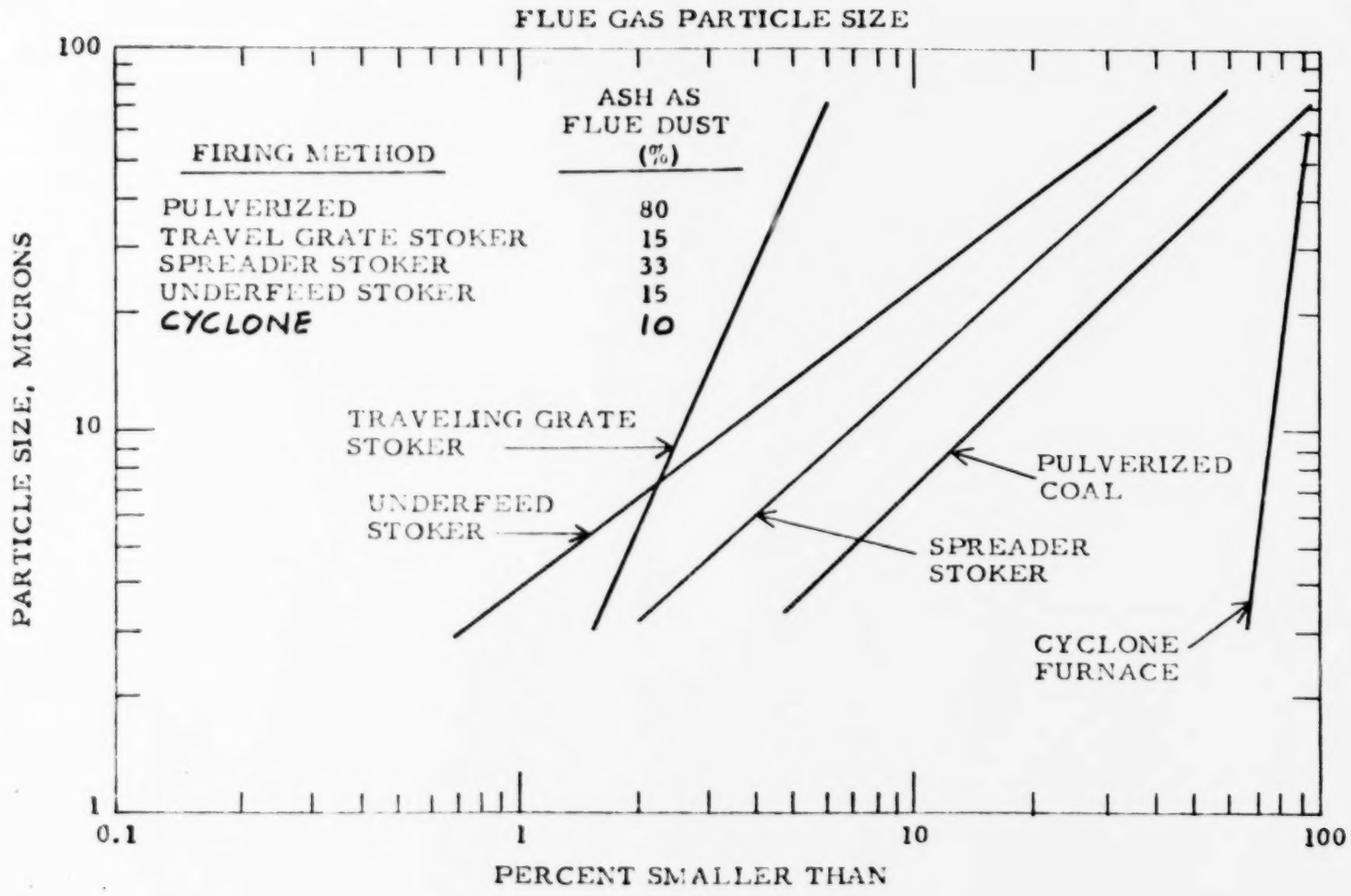



Figure 6. Distribution of Fly Ash for Different Firing Methods

Table 9 shows a comparison of various dust collecting equipment. In many power stations a combination of a mechanical cyclone collector and an electrostatic precipitator is used for a 99%+ particle collection efficiency. The size of this equipment is large. The need for removal of fly ash from the gases prior to the scrubbing step is an important consideration; it is further analyzed in Section C, below.

B. COMPARATIVE STUDIES ON REDUCTION STEP

The operating and capital costs for the process for an 800 Mwe power plant were estimated, and a trade-off analysis was conducted to determine the effect of the reduction step on the overall cost of the process. The comparisons in this study are based on the following:

1) Plant size - 800 Mwe
2) Coal sulfur content - 3%
3) Flue gas treated - 88 x $10^6$ SCFH
4) Plant factor - 90%
5) Process removal of sulfur oxides - 95%
6) Mole ratio of carbonate to sulfite in absorber - 3:1
7) 10% of sulfite oxidizes to sulfate in absorber, the remainder disproportionates in the heater to form sulfide and sulfate.

1. Utility Requirements

This study compares the economics of utilizing hydrogen, hydrogen/carbon monoxide mixtures, and carbon as the reducing agent. It was assumed that 80% of the theoretical hydrogen or carbon monoxide requirements could be effectively utilized. The studies are based on using a reaction temperature of 600°C when using a gas reactant, and a reaction temperature

**TABLE 9**

BASIC TYPES OF PARTICLE COLLECTION EQUIPMENT

| COLLECTOR TYPE | NORMAL PARTICLE SIZE RANGE | TYPICAL ΔP-inch w.g. | APPROX. POWER kw/1000 cfm |
|---|---|---|---|
| 1. GRAVITY SETTLING CHAMBER | COARSE +100μ | 0.1-0.5 | 0.1 |
| 2. MECH. COLLECTORS-CYCLONES | MEDIUM-COARSE | | |
| SMALL DIA | 10-100μ+ | 1-5 | 0.2-1 |
| LARGE DIA | MEDIUM-COARSE | 1-5 | 0.2-1 |
| 3. SCRUBBERS | | | |
| LOW ENERGY | MEDIUM-COARSE | 5-15 | 1-3 |
| HIGH ENERGY | FINE-MEDIUM 0.1-10μ | 30-50 | 6-10 |
| 4. BAG FILTERS | VERY FINE-MED. 0.1-100μ+ | 3-6 | 0.6-1.2 |
| 5. ELECTROSTATIC PRECIPITATORS | VERY FINE-MED. MOST EFFECTIVE <20μ | 0.1-0.5 | 0.2-0.5 INCL. EL. POWER |

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of 700°C when carbon is the reducing agent. The higher temperature was necessitated by the slow carbon reduction rate at lower temperatures. Based on the above assumptions, the flow rate into the reducer is 886 lb/min of sulfate, 135 lb/min of sulfide, and 1670 lb/min of carbonate, and $16.9 \times 10^6$ SCF per day of hydrogen. The costs associated with producing the hydrogen were based on information from C & I Girdler Corp. Approximately 90% of the utility cost to produce the reducer gas can be attributed to the cost of natural gas. For cost comparison, a plant producing 71% $H_2$ and 25% carbon monoxide was included. Table 10 compares the hydrogen and hydrogen-carbon monoxide costs and also shows the cost of the associated equipment to manufacture the reducer gas. Columns 1 and 2 compare the effect of natural gas costs of 40 and 50¢ per 1000 SCF. Columns 3 and 4 show the respective comparisons when a reformer gas mixture of 71% hydrogen and 25% carbon monoxide is used. The cost of natural gas influences the economics substantially. The price of 40¢/1000 SCF should apply to the majority of plants.

TABLE 10

REDUCER GAS COST

| Column | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Reducer Gas | 96% $H_2$ | 96% $H_2$ | 71% $H_2$ - 25% CO | 71% $H_2$ - 25% CO |
| Nat. Gas SCF/1000 SCF Dry Gas | 515 | 515 | 400 | 400 |
| Nat. Gas Cost/1000 SCF (¢) | 40 | 50 | 40 | 50 |
| Reducer Gas Cost/ 1000 SCF (¢) | 23.2 | 28.5 | 17.6 | 21.6 |
| Gas Cost/Yr ($10^6$ $) | 1.29 | 1.59 | 0.975 | 1.2 |
| Equipment Cost ($10^6$ $) | 2.5 | 2.5 | 2 | 2 |

Using these cost figures and adding the interest during construction, working capital and maintenance (3% of depreciation base) leads to the total cost attributable to the reducer gas generation summarized in Table 11. All equipment is capitalized at 14% of total investment. Also shown in Table 11 for comparison are the utility costs prepared for the Summary Report (column 5). For that report the coal-steam reaction was used to prepare the reducer gas. The columns of Table 11 are extended from Table 10.

TABLE 11

TOTAL CHARGE FOR REDUCER GAS PRODUCTION

| Column (from Table 10) | 1 | 2 | 3 | 4 | 5* |
|---|---|---|---|---|---|
| Reducer Gas | 96% $H_2$ | 96% $H_2$ | 71% $H_2$/25% CO | 71% $H_2$/25% CO | Coal-steam g |
| Utilities ($10^6$ \$/yr) | 1.29 | 1.59 | 0.975 | 1.2 | 0.720 |
| Capital Charges ($10^6$ \$/yr) | 0.382 | 0.382 | 0.305 | 0.305 | 0.133 |
| Maintenance ($10^6$ \$/yr) | 0.077 | 0.077 | 0.06 | 0.06 | 0.027 |
| Total Charge for Gas ($10^6$ \$/yr) | 1.749 | 2.049 | 1.3 | 1.565 | 0.890 |
| Total Charge for Gas (mils/kwh) | 0.276 | 0.323 | 0.205 | 0.247 | 0.1405 |
| Increase from Summary Report (mils/kwh) | 0.1355 | 0.1815 | 0.065 | 0.106 | |

* Costs from Summary Report, June 1, 1967 - Feb. 29, 1968 (AI-68-104)

2. Comparison Between Reducer Gas Production and Utilization of Carbon

It is estimated that 41,300 tons per year of carbon is required for the reduction step in an 800 Mwe power plant. If petroleum coke is used, the cost is estimated to be \$7 per ton, delivered. Adding an extra \$100,000 for coke handling equipment, a yearly charge of \$304,000 results. Table 12

compares the various gas reduction steps with the coke process and shows the total additional investment that can be made before breakeven occurs. As will be shown later, additional costs for the reducer, heater and heat exchanger can be expected due to the higher operating temperature.

TABLE 12

REDUCTION COST COMPARISON

| Column (from Table 10) | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Reducer Gas | 95% $H_2$ | 96% $H_2$ | 71% $H_2$/25% CO | 71% $H_2$/25% CO |
| Total Charge for Gas ($10^6$ $) | 1.749 | 2.049 | 1.3 | 1.565 |
| Coke Cost ($10^6$ $) | 0.304 | 0.304 | 0.304 | 0.304 |
| Cost Reduction ($10^6$ $) | 1.445 | 1.745 | 0.996 | 1.261 |
| Cost Reduction (mils/kwh) | 0.228 | 0.276 | 0.157 | 0.199 |
| Additional Investment Available for Breakeven (14% Capital Charge) ($10^6$ $) | 10.25 | 12.5 | 7.5 | 9.1 |

An interesting comparison of the three reduction processes is to compute the reduction agent cost per ton of sulfur produced. Theoretically for every ton of sulfur produced, 1/6 ton of hydrogen, 2-5/8 tons of carbon monoxide or 9/16 ton of carbon are required. An 800 Mwe plant, based on the assumption previously stated, can produce 63,200 tons of sulfur per year. Based on natural gas costs of 40¢ per 1000 SCF, Table 13 compares the three reducing agents studied.

TABLE 13

REDUCING AGENT COST COMPARISON

| Reducing Agent | Cost per Ton of Sulfur Produced ($) |
|---|---|
| Hydrogen | 23.50 to 27.50 |
| Hydrogen-Carbon Monoxide (71/25) | 20.50 |
| Carbon (Fluidized Coke) | 4.80 |

All of the above trade-off studies are not complete until they include the differential in the reducer cost. Also, any differential development cost and the state of technology has to be taken into consideration. Since the last overall cost for an 800 Mwe plant was estimated (Summary Report), several modifications were made and new cost information was obtained. In conjunction with this study, therefore, overall system costs were recalculated; they are presented below.

3. Equipment and Operating Costs of an 800 Mwe Sulfur Dioxide Removal Process

The investment cost for the absorber regenerator portion of the process for hydrogen or a 71/25 mixture of hydrogen/carbon monoxide is $\$5.226 \times 10^6$ and $\$5.346 \times 10^6$ respectively, as was shown in Table 6, Section II-D. As a comparison, the cost for the absorber-regenerator equipment, using carbon in the form of fluidized coke, is estimated at $6,654,000. The increase in equipment cost is mainly attributable to the higher temperature requirements (700°C) for the reducer, heater and heat exchanger, and an increase from 1 hour to 1-3/4 hours for the reduction reaction time. The total investment, however, is somewhat less since the reduction gas producer

is eliminated. Table 14 compares the capital costs for carbon reduction and hydrogen reduction. This table includes the cost for a Claus sulfur plant.

TABLE 14

TOTAL ESTIMATED CAPITAL REQUIREMENTS
($10^3$ $)

| Item | Costs ($H_2$ Red'n) | Costs (C Red'n) |
|---|---|---|
| Absorber-Regenerator | 5,226 | 6,654 |
| Coke Handling | | 100 |
| Reduction Gas Producer | 2,500 | |
| Sulfur Recovery | 1,780 | 1,780 |
| Plant Facilities | 470 | 420 |
| Plant Utilities | 665 | 590 |
| Total Construction | 10,641 | 9,544 |
| Initial Charge | 95 | 105 |
| Total Plant Cost | 10,736 | 9,649 |
| Interest During Construction | 255 | 232 |
| Subtotal for Depreciation | 10,991 | 9,881 |
| Working Capital | 695 | 620 |
| Total Investment | 11,686 | 10,501 |

Table 15 compares the estimated annual and net operating costs for the carbon reduction and hydrogen reduction processes.

TABLE 15

ESTIMATED ANNUAL AND NET OPERATING COSTS*
($10^3$ $)

| Item | ($H_2$ Red'n) | Revision 3 (C Red'n) |
|---|---|---|
| Direct Cost | | |
| Raw Materials and Utilities | | |
| Absorbent | 83 | 83 |
| Reducing Agent | 1,290 | 290 |
| Power Water Heat | 158 | 158 |
| Subtotal | 1,531 | 531 |
| Direct Labor | | |
| 72 mh/day x 2.75/mh | 83 | 83 |
| Plant Maintenance (3% of Depreciation Base) | 328 | 295 |
| Payroll Overhead (18.5% of Payroll) | 63 | 57 |
| Operating Supplies (20% of Plant Maint.) | 65 | 59 |
| Total Direct Cost | 2,070 | 1,025 |
| Indirect Cost (50% Labor, Maintenance, and Supplies) | 238 | 218 |
| Total Capital Charges (14% of Total Invest.) | 1,632 | 1,466 |
| Net Operating Cost ($) | 3,940 | 2,709 |
| Net Operating Cost (mils/kwh) | 0.622 | 0.428 |

* No sulfur credit, flue gas stack reduction credit, or corrosion reduction credit

4. Significance of Reduction Step

Table 16 summarizes the costs associated with the reduction step for the three main cases studied, and compares them with costs previously estimated. Hydrogen cost was based on the availability of natural gas at 40¢/1000 SCF. As can be seen from this table, costs attributable to the reduction step are very significant. Forty seven percent of the net operating cost can be attributed to the reduction step when hydrogen is used. This high fraction can be significantly lowered (to 23%) using carbon. However, the costs presented for carbon are based on several assumptions that require further verification. The reducer was sized on the basis that the reaction time is 1-3/4 hours at 1292°F (700°C). This leads to a vessel size 75% larger. In addition, the price of procuring the vessel for the higher temperature was increased by a factor of two. The metallurgy and chemistry both require further effort, especially the material requirements, effect of carbon, and the thermal requirements of the reaction. No costs were included for supplying additional heat during the endothermic carbon reduction step. However, the heater costs were increased by the proportional temperature increase requirement plus a factor of two for material cost increases. Further effort is needed to determine the best methods for heating the fluid to the higher temperature and supplying heat to compensate for the endothermic reaction.

TABLE 16

COSTS ATTRIBUTABLE TO REDUCTION STEP
($10^3$ $/yr)

| Item | 96% + $H_2$ 40¢ Nat'l Gas | 71/25 $H_2$/CO 40¢ Nat'l Gas | Carbon |
|---|---|---|---|
| Coal | | | 290 |
| Raw Materials for $H_2$ | 1,290 | 975 | |
| Reducer Gas Man. Equip. | 382 | 305 | 14 |
| Maintenance Man. Equip. | 77 | 60 | 2 |
| Reduction Equipment | 73 | 87 | 249 |
| Maintenance Equipment | 16 | 16 | 43 |
| Payroll Overhead | 15 | 16 | 8 |
| Total Reduction Cost | 1,853 | 1,459 | 606 |
| Percent of Total Annual Cost | 47 | 41 | 23 |

5. Credits for Removing Sulfur Oxides

The above costs were presented without taking credits for savings or production of sulfur. In order to complete the study, the following credits should be deducted from the operating cost to arrive at the true costs:

a) A credit of $1.12 per installed kilowatt is possible when the stack height is reduced from 800 to 300 ft.[3] For an 800 Mwe plant this amounts to $895,000 in capital equipment.

b) Combustion Engineering[3] has estimated that elimination of sulfur dioxide will reduce corrosion, and credits 5.3¢/ton of coal fired for this. This would allow a credit of $132,500 per year. Combined with item (a), this would in effect reduce the net operating cost 0.04 mils/kwh.

c) The plant can produce 63,200 tons of sulfur per year. Based on a selling price of $40 per ton, $2,530,000 in revenue, equivalent to 0.4 mil/kwh, can be realized

Table 17 shows the net operating cost (profit) when the above credits are taken into consideration.

TABLE 17

NET OPERATING COSTS OF DESULFURIZATION PROCESS
(Plant Capacity - 800 Mwe)

| | 90% Plant Factor | | |
|---|---|---|---|
| | $H_2$ Red'n | $H_2$/CO Red'n (71/25) | C Red'n |
| Net Operating Cost Before Credit (mils/kwh) | 0.622 | 0.56 | 0.428 |
| Credit for Stack Gas Size Reduction and Corrosion Reduction (mils/kwh) | 0.04 | 0.04 | 0.04 |
| Sulfur Credit ($40/ton) | 0.40 | 0.40 | 0.40 |
| Net Operating Cost (Profit) After Credit (mils/kwh) | 0.182 | 0.120 | (0.012) |

## C. COMPARATIVE STUDIES OF FLY ASH REMOVAL

The problem caused by fly ash has been examined both technologically and economically, and possible solutions considered. Coal-fired boilers produce large amounts of fly ash, which will be carried along with the flue gases into the carbonate scrubber unless it is removed first. It can be expected that all of the fly ash which enters the scrubber will be picked up by the molten carbonate, and incorporated into the process melt. Previous work has shown that only the calcium and iron constituents of the ash are soluble to any extent in the melt; the solubilities of these two are slight and do not interfere with the process. However, a continuous buildup of fly ash would soon turn the melt into a slurry or paste, which could not be circulated through the process equipment. Therefore, the fly ash must be prevented from accumulating in the melt. This can be done by removing it from the gas stream before it enters the scrubber, or by removing it from the melt, or both. Economic considerations will determine the proper method. For the purpose of the study, it was assumed that the ash content of the coal to be fired is 10%, and that 80% of the ash will be carried as fly ash in the exhaust gas stream. Consideration of the properties of fly ash and the quantity of fly ash involved led to the requirement of an electrostatic precipitator in the gas stream prior to the scrubbing step. This study compares the overall cost effectiveness of using electrostatic precipitators with a fly ash removal efficiency of 95%, 99%, and 99.9%. It was assumed that all of the fly ash not collected in the electrostatic precipitator was removed in the scrubber when contacted with the molten carbonate.

1. Cost Comparison of Electrostatic Precipitators

For an 800 Mwe installation, a cost and size comparison of electrostatic precipitators of fly ash, at a flue gas design temperature of 800°F, was prepared. The comparison was based on fly ash removal efficiencies of 95%, 99%, and 99.9%. Table 18 shows this comparison and includes the cost for treating a 320°F flue gas at a 99% efficiency. These data were obtained from the Western Precipitation Group of the Joy Manufacturing Co., and also substantiated by Research-Cotrell, Inc.

TABLE 18

COMPARISON OF ELECTROSTATIC PRECIPITATORS
800 Mwe Size - 800°F

| Efficiency (%) | Size | Installed Cost* ($10^6$ $) |
|---|---|---|
| 95 | 184' wide, 21' deep x 35' high | 2 |
| 99 | 210' wide, 29' deep, 35' high | 3 |
| 99.9 | 222' wide, 42' deep, 35' high | 4.5 |
| 99 | Gases at 320°F | 1.5 |

* Complete with electrical equipment, heat insulation and support steel.

An additional 15 ft of height must be provided for hoppers below the collection equipment, and 7 ft must be provided for electrical equipment above the collection equipment. Electrical consumption is approximately 800 kw for a 95% removal efficiency, 1500 kw for a 99% removal efficiency, and 2400 kw for a 99.9% removal efficiency. The electrical consumption cost was evaluated at 2.8 mils/kwh.

An 800 Mwe plant fired with pulverized coal will produce 54,000 lb/hr of fly ash (based on 10% ash in coal, 80% of ash carried as fly ash). Other firing methods or coal types will vary this quantity. The gas flow through the electrostatic precipitator for this plant is $3.4 \times 10^6$ cu ft/min at the 800°F condition.

2. Melt Loss

It has been found that the particle density of fly ash is approximately twice that of its bulk density. With a dry ash porosity of approximately 0.5, it is estimated that for each pound of fly ash in contact with molten carbonate, a pound of the melt is absorbed and held in the filter cake. The constituents of the filter cake can be anticipated to be 40% carbonate, 10% sulfate, and 50% ash. The molten carbonate consists of 32% $LiCO_3$, 33% $Na_2CO_3$, and 35% $K_2CO_3$. Dependent on the efficiency of the fly ash removal prior to the absorption step, a wide variation in the quantity of molten liquid can be held in the fly ash. For example, a 99% efficient precipitator will allow 540 lb/hr of melt to be absorbed, and a 95% efficient precipitator will allow 2700 lb/hr of melt to be absorbed. The cost of this mixture is influenced predominantly by the high cost of lithium carbonate, with a cost ratio of 26:1:5 of the respective lithium, sodium, and potassium constituents. The eutectic cost has been estimated at 22¢/lb at the quantities required. If the molten carbonate and sulfate are not recovered from the filter cake, the replacement cost, based on an 80% load factor, is as shown in Table 19.

TABLE 19

CARBONATE REPLACEMENT COST

| Fly Ash Precipitator Efficiency (%) | $M_2CO_3$ Replacement Quantity (lb/yr) | $M_2CO_3$ Replacement Cost ($/yr) | $M_2CO_3$ Replacement Cost (mils/kwh) |
|---|---|---|---|
| 99.9 | $3.7 \times 10^5$ | $1.1 \times 10^5$ | 0.0148 |
| 99 | $3.7 \times 10^{6*}$ | $1.1 \times 10^6$ | 0.148 |
| 95 | $18.5 \times 10^6$ | $5.5 \times 10^6$ | 0.74 |

* $3.7 \times 10^6$ lb of $M_2CO_3$ per year is 100 carloads per year.

As can be seen from Table 19, the carbonate replacement cost is considerable at less than high fly ash precipitation efficiencies. Preliminary investigations are therefore being conducted to find economic schemes for recovering the molten carbonate from the filter cake.

3. Process Filter Costs

The capacity of the filter will be directly dependent on the amount of fly ash previously removed in the electrostatic precipitator and the allowed time between cleanup or backwash operation. Selection of the filter element is now under experimental investigation.

For the purpose of this study a Croll-Reynolds ClaRite Filter was chosen. The ClaRite filter consists of a pressure vessel with permanent tubular filter elements suspended from a tubesheet. The elements are constructed of wedge-shaped wire helically wound around longitudinal stiffening rods. It is expected that the fly ash will act as its own filter aid, and that the filter cake can be removed by backwashing, vibration or ultrasonic cleaning. Units would be placed in parallel for continuous

operation. The size of the units was estimated on an 8 and 24-hr operation cycle. At the 95% and 99% precipitator efficiencies, the amount of filter cake is very large and sets the practical limitation on an 8-hr cycle.

The following are the requirements for the various electrostatic precipitator efficiencies:

| Precipitator Efficiency (%) | 99.9 | 99 | 95 |
|---|---|---|---|
| Loading on Filter in 8 hr ($ft^3$) | 7.1 | 71 | 355 |
| Loading on Filter in 24 hr ($ft^3$) | 21.6 | 216 | 1080 |

A Model 42-270 is quoted with a cake capacity of 21.3 $ft^3$, and a Model 48-475 is quoted with a cake capacity of 37.7 $ft^3$. Based on these models, and an estimated price of $50,000 per unit for the former, and $90,000 per unit for the latter, the total cost was established.

4. Overall Comparison

Table 20 lists the various costs involved in removing the fly ash for the three different precipitator efficiencies. All costs are given on a mils/kwh basis, assuming capitalization of the equipment costs at 14% per year.

TABLE 20

FLY ASH REMOVAL COSTS

| Precipitator Efficiency (%) | 95 | 99 | 99.9 |
|---|---|---|---|
| Precipitator Cost, Total (mils/kwh) | 0.0500 | 0.0750 | 0.1125 |
| Electricity Cost (mils/kwh) | 0.0028 | 0.0052 | 0.0084 |
| Carbonate Replacement Cost (mils/kwh) | 0.7400 | 0.1480 | 0.0148 |
| Filter Cost (8-hr Cycle) (mils/kwh) | 0.0450 | 0.0090 | 0.0024 |
| Total Cost Without Carbonate Recovery (mils/kwh) | 0.8378 | 0.2372 | 0.1381 |

These costs also show that without a carbonate recovery process, the lowest overall cost is achieved by the highest precipitator efficiency. However, it is also possible to estimate the maximum effect of carbonate recovery by calculating the costs for a free, 100% efficient recovery process. With this assumption, the costs of Table 20 are reduced by the total carbonate replacement cost. The results are listed in Table 21.

TABLE 21

MINIMUM COSTS WITH CARBONATE RECOVERY

| Precipitator Efficiency (%) | 95 | 99 | 99.9 |
|---|---|---|---|
| Total Cost w/o Carbonate Recovery (mils/kwh) | 0.8378 | 0.2372 | 0.1381 |
| Carbonate Replacement Credit (mils/kwh) | 0.7400 | 0.1480 | 0.0148 |
| Total Cost with Free Carbonate Recovery (mils/kwh) | 0.0978 | 0.0892 | 0.1233 |

These data indicate that (1) there is little incentive to recover the carbonate if a 99.9% efficient precipitator is used, (2) the carbonate recovery process must be inexpensive and efficient, or else it will be cheaper to use a 99.9% efficient precipitator and discard the filter cake, and (3) even with a free, 100% efficient carbonate recovery system, a precipitator with an efficiency greater than 95% should be used.

The above costs are based on vendor information, and on the assumption that the efficiencies quoted can be met and maintained. No penalty for the space required for the precipitator was assessed. However, the total cost of the precipitator was charged; if only the excess cost over a standard, low-temperature precipitator is charged, the costs should all be decreased by 0.0375 milw/kwh.

5. Melt Recovery

One proposed method to recover the melt is to displace the melt out of the cake with some cheaper liquid, and then discard or process the resulting mixture. However, the material used to displace the melt will have to be liquid at 800-850°F, and be very inexpensive. It will also have to be compatible with the process; i.e., not interfere if some gets into the process stream. Molten sodium hydroxide has been suggested for this; however, it is corrosive and difficult to handle at the high temperatures required.

It should also be possible to recover the melt from the cake by an aqueous process. The sodium and potassium components of the melt are water soluble, so they can be recovered in aqueous solution by slurrying the cake with water and refiltering. The lithium carbonate, however, is only slightly soluble, so it cannot be recovered by dissolving it without using an excessive amount of water. It is too valuable to be discarded, since it makes up over 80% of the value of the salt. Therefore, a chemical treatment is required to convert the lithium carbonate into a more soluble form. Several processes have been proposed for this. They are described in Part V of this **Progress Report**. A complete economic evaluation of all melt recovery processes will be done in the future.

## V. REFERENCES

1. Katell S.. Chem. Eng. Progress 62, p. 67 (Oct., 1966)

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